



Short communication

Different proportions of C/KCu₇S₄ hybrid structure for high-performance supercapacitors

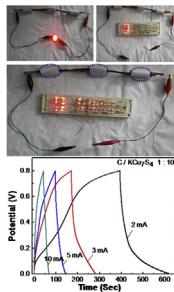
Shuge Dai, Yi Xi*, Chenguo Hu, Xule Yue, Lu Cheng, Guo Wang

Department of Applied Physics, Chongqing University, Chongqing 400044, PR China

HIGHLIGHTS

- KCu₇S₄ has the channels structure, minor resistance and good electrochemical property.
- The changed KCu₇S₄ electrode structure improve its electrochemical performance.
- Constructing a hybrid C/KCu₇S₄ for ECs. The hybrid ECs demonstrate outstanding electrochemical performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 January 2014

Received in revised form

25 February 2014

Accepted 28 March 2014

Available online 13 April 2014

Keywords:

C/KCu₇S₄

Hybrid structure

Different proportions

Supercapacitors

ABSTRACT

KCu₇S₄ has the channel structure and minor resistance. Its double larger channels ensure that the ions can well exchange with other's, at the same time, can shorten the ionic diffusion path and improve the ionic and electronic transport. So KCu₇S₄ shows good electrochemical property. The paper reports a novel and high performance supercapacitor based on hybrid carbon particles and KCu₇S₄ (C/KCu₇S₄) electrode. For the hybrid structure with different proportions of C and KCu₇S₄, the C/KCu₇S₄ (1:10) hybrid supercapacitor shows preferable electrochemical performance and large specific capacitance (469 mF cm⁻²) at high charge–discharge rate (2 mA), still retaining ~95% of the capacitance over 5000 cycles by charge–discharge process at a fixed current of 10 mA. Three supercapacitor units in series can light 50 light-emitting diodes (LEDs) for 2.5 min, 10 LEDs for 4 min, one LED for 5.5 min. The much-increased capacity, rate capability, and cycling stability may be attributed to the superionic conductive KCu₇S₄ nanowires and C/KCu₇S₄ hybrid structure, which improve ionic and electronic transport, enhance the kinetics of redox reactions through the electrode system.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Supercapacitors have attracted considerable interest as energy storage devices in recent years. They are widely used to power electric and hybrid electric vehicles. The performances of the supercapacitors are largely dependent on the property and

structure of the electrode materials [1]. It has been well established that electrodes with proper nanostructures may enhance not only the power density but also the cycling stability. At the same time, superionic conductive materials are solids that their ionic conductivity is similar to those found in ionic liquids, with applications in electrochemical energy storage devices [2–4].

The structure of KCu₇S₄ is similar to that of alfa-MnO₂, which consists of a compound in which one species form pseudo-one-dimensional channels and the K⁺ cations occupy the channels. Because of its double larger channels structure, it not only enhances

* Corresponding author. Tel.: +86 23 65678362; fax: +86 23 65678262.

E-mail addresses: xyi6@cqu.edu.cn, xiyi.xi@163.com (Y. Xi).

the ionic and electrons transportant, but also shortens the ionic diffusion path. When it is applied across the electrodes, the K^+ ions can well exchange with Li^+ ions. So, it exhibits preferable electrochemical properties. In addition, at room temperature, its structure is consistent with doubling of the lattice along the c axis [5], and the conducting pathway is primarily along the c axis [6], which is in accordance with the superion conduction [7]. So, it displays an extremely high ionic conductivity. The KCu_7S_4 nanowire ECs has been reported and it shows a good electrochemical performance with a large specific capacitance 570 F g^{-1} at a scan rate of 1 mV s^{-1} [8].

To improve the electrochemical performance of the KCu_7S_4 nanowires ECs, it also can change the KCu_7S_4 electrode structure, hybrid materials, and their composition. The hybrid electrochemical capacitors, which usually combine one battery-type faradaic electrode (as energy source) with the other capacitive electrode (as power source) in the same cell [9,10]. It has many advantages in terms of device fabrication, stability, excellent electrochemical properties (high conductivity and wide potential window). Moreover, a wide variety of hybrid ECs have been created and tested, it still displays a grand challenge to identify the most promising structure or architecture that dramatically enhance the capacity while maintaining the excellent rate capability and charge–discharge cycling life [10].

Here, we demonstrate a novel superionic conductive KCu_7S_4 nanowires material, and it shows a good electrochemical property. When a voltage was applied across the electrode, the K^+ ions would exchange with Li^+ ions along the c axis path [6]. The cathodic and anodic currents nearly trend to zero at a scan range of $0\text{--}0.4\text{ V}$ of the KCu_7S_4 electrode under the low speed scan, which is in accordance with the superion conduction [7]. We also present an alternative route by constructing a hybrid carbon particles and KCu_7S_4 nanowires (C/KCu_7S_4) for ECs. Because of the high pseudocapacitance of KCu_7S_4 nanowires [8], and the good stability and conductivity of carbon particles, we can achieve high performance for capacitors by exploring the mixing ratio of carbon particles and KCu_7S_4 nanowires. Experimental results show that the C/KCu_7S_4 hybrid ECs (1:10) demonstrates outstanding electrochemical performance with large specific capacitance of 469 mF cm^{-2} (300 F g^{-1}) at high charge–discharge rate of 2 mA , the highest energy density of 8.14 mWh cm^{-3} and the maximum power density of 664.4 mW cm^{-3} at high charge–discharge rate of 2 mA . The good electrochemical stability has been demonstrated by 5000 cycles of rapid charge–discharge at 10 mA , with only a capacitance decline of 5%. Moreover, we have connected three hybrid ECs units in series to light a light-emitting diode (LED) for 5.5 min, 10 light-emitting diodes (LEDs) for 4 min, and 50 light-emitting for 2.5 min. (Supporting information Fig. S2). All the experimental results indicate the optimistic prospect of using C/KCu_7S_4 hybrid nanostructure as supercapacitor electrode materials.

Supplementary video related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.138>.

2. Experimental section

2.1. Synthesis of the KCu_7S_4 nanowires

Single-crystalline KCu_7S_4 nanowires were synthesized by hydrothermal method, which was reported elsewhere [8].

2.2. Assembly of the solid-state supercapacitor

Firstly, C and KCu_7S_4 nanowires were mixed evenly by varying the weight ratio (1:5, 1:8, 1:10 and 1:15). Secondly, the mixture of

C/KCu_7S_4 was pressed into thin films in 10 MPa with laminator, and then the C/KCu_7S_4 film was fixed in the carbon block with fulmargin. Finally, the supercapacitors were assembled by two pieces of C/KCu_7S_4 hybrid electrodes with a separator (Whatman $8\text{ }\mu\text{m}$ filter paper) sandwiched in between and polyvinyl alcohol PVA–LiCl gel as a solid electrolyte. PVA–LiCl gel electrolyte was simply made as follows: 12.6 g LiCl was mixed with 60 mL deionized water and then 6 g of PVA power was added. The whole mixture was heated to $85\text{ }^\circ\text{C}$ under vigorous stirring until the solution become clear. Then the solution was keep at $85\text{ }^\circ\text{C}$ without stirring [11]. Before the assembling, the C/KCu_7S_4 hybrid electrodes were immersed into the PVA–LiCl solution for 5 min [12]. They were then assembled one by one and kept at room temperature. After the PVA–LiCl gel solidified, the solid-state supercapacitors were prepared.

2.3. Characterization

The method of characterization was reported elsewhere [8]. In brief, the morphologies, chemical composition, and the structure of the products were characterized by field-emission scanning electron microscopy (Nova 400 Nano SEM) and XRD (BDX3200 China). The electrochemical properties of three kinds of electrodes were investigated with CV and charge–discharge measurements in a conventional three-electrode cell employing a CHI 760D electrochemical workstation.

3. Results and discussion

3.1. Characterization of the electrocatalysts

Fig. 1 shows the XRD patterns of prepared KCu_7S_4 nanowires and C/KCu_7S_4 hybrid nanostructure. From the pattern A, we know that the sample is KCu_7S_4 . As shown in the pattern B, all of the C diffraction peaks match the C structure (PDF: 41-1487), with the lattice constants $a = 2.47\text{ \AA}$, $b = 2.47\text{ \AA}$, $c = 6.724\text{ \AA}$. So we can know that the carbon particles were mixed into the KCu_7S_4 nanowires film. The SEM image of the KCu_7S_4 nanowires is presented in Fig. 2a, the diameter of about $2\text{ }\mu\text{m}$ and the length up to $110\text{ }\mu\text{m}$. The size of the carbon particles is about $5\text{--}15\text{ }\mu\text{m}$. The SEM images of the C/KCu_7S_4 hybrid nanostructure with the different weight ratio of C to KCu_7S_4 nanowires (1:5, 1:8, 1:10 and 1:15) were presented in Fig. 2b, c, d and e, respectively.

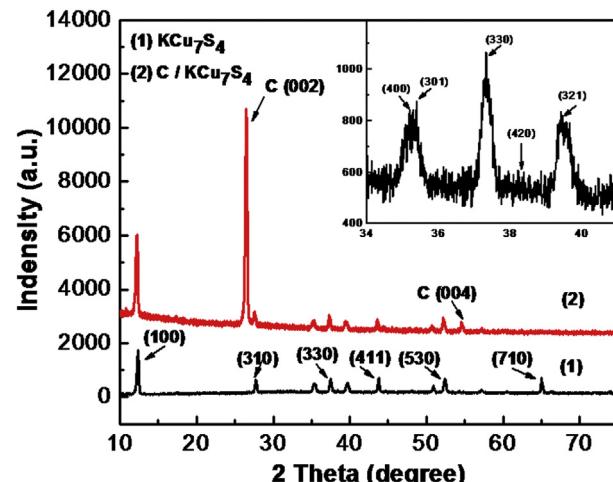


Fig. 1. XRD patterns of prepared KCu_7S_4 nanowire, and C/KCu_7S_4 hybrid electrodes.

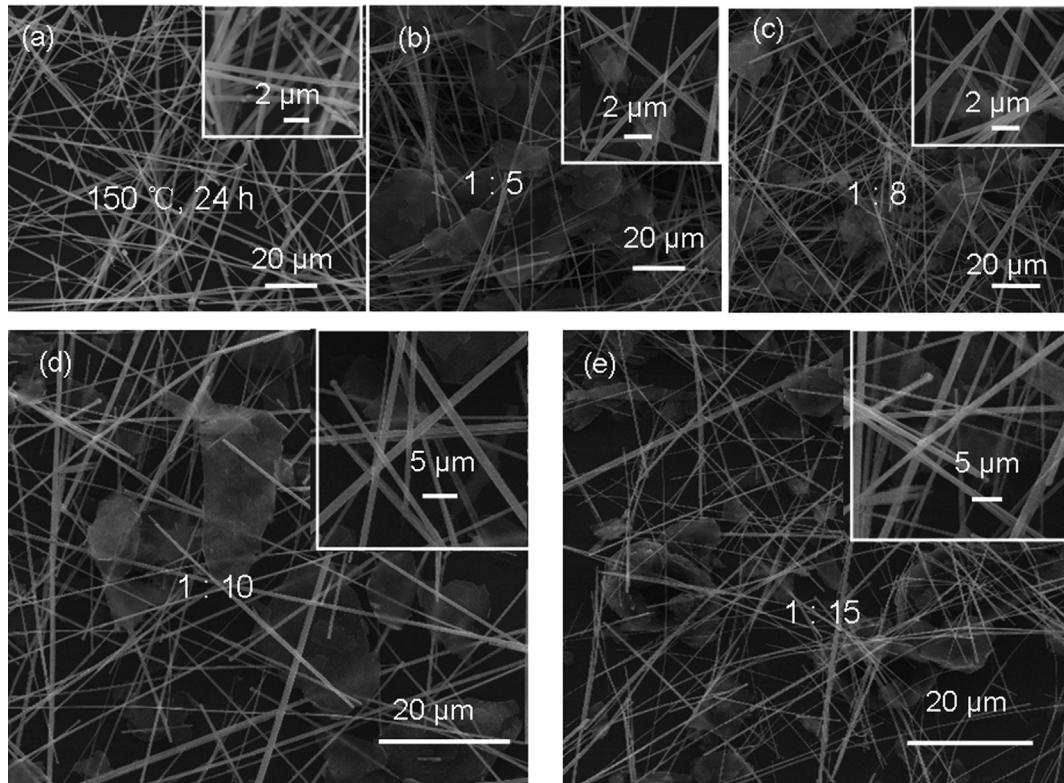


Fig. 2. (a) SEM images of prepared KCu₇S₄ nanowires. (b), (c), (d) and (e) SEM images of the C/KCu₇S₄ hybrid nanostructure with the different weight ratio of C to KCu₇S₄ nanowires (1:5, 1:8, 1:10 and 1:15).

3.2. Performance of hybrid supercapacitors

Fig. 3a displays CV curve of the KCu₇S₄ nanowires electrode at a scan rate of 0.5 mV s⁻¹ with potential windows ranging from 0 to

0.8 V. There is a cross at 0.45 V in the CV curve, and the cathodic and anodic currents nearly trend to zero at a scan range of 0–0.4 V. This reason is that the KCu₇S₄ lattice is composed of a three-dimensional Cu–S framework which contains pseudo-one-

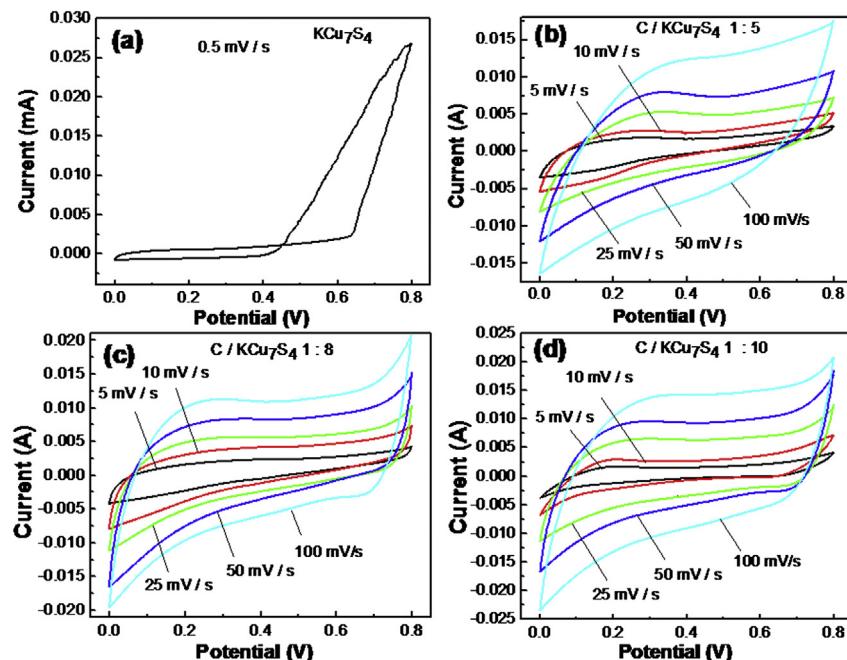


Fig. 3. (a) CV curve of KCu₇S₄ nanowires electrode at a scan rate of 0.5 mV s⁻¹ (b), (c) and (d) CV curves of C/KCu₇S₄ hybrid ECs at various scan rates by varying the weight ratio of C to KCu₇S₄ nanowires (1:5, 1:8 and 1:10).

dimensional channels in which the K^+ cations reside [6]. Its structure is consistent with doubling of the lattice along the c axis [8], and the conducting pathway is primarily along the c axis [6], which is in accordance with superion conduction [7]. While Copper (I) sulphide close to their critical temperature, which exhibits superionicity. Fig. 3b, c and d shows CV curves of the C/KCu₇S₄ hybrid ECs at various scan rates with potential windows ranging from 0 to 0.8 V by varying the weight ratio of C to KCu₇S₄ nanowires (1:5, 1:8 and 1:10), all of the CV curves exhibit approximately box-like shapes with a mirror-image feature, and the shapes of these CV curves do not significantly change as the scan rate increased from 5 to 100 mV s⁻¹, revealing the ideal capacitance behaviors and good high-rate capabilities of C/KCu₇S₄ hybrid ECs [12]. CV curves of the C/KCu₇S₄ hybrid ECs with potential windows ranging from 0 to 0.8 V by the weight ratio of C to KCu₇S₄ nanowires (1:15) also can be seen in Fig. S1a. The capacitance of the C/KCu₇S₄ hybrid ECs (1:10) was higher than those for C/KCu₇S₄ hybrid ECs (1:5, 1:8 and 1:15). For example, the capacitance of the C/KCu₇S₄ hybrid ECs (1:10) was achieved 490 mF cm⁻² (~ 313 F g⁻¹) at a scan rate of 5 mV s⁻¹, which was higher than the C/KCu₇S₄ hybrid ECs 383 mF cm⁻² (1:5, ~ 245 F g⁻¹), 401 mF cm⁻² (1:8, ~ 256 F g⁻¹) and 446 mF cm⁻² (1:15, ~ 285 F g⁻¹), and the results are shown in Fig. 4a. Such superior performances of the C/KCu₇S₄ hybrid ECs can be attributed to the follow factors. Firstly, the C particles have the large specific surface and good electrical conductivity, so they can not only expand the penetration area of the electrolyte and the C/KCu₇S₄ hybrid electrodes, but also shorten the ion diffusion path, enhance ionic and electronic transport through the electrode system. Secondly, if the ratio of the C to KCu₇S₄ was too small, the electrodes would have poor conductivity, and then the capacitor would have larger internal resistance. If the ratio of the C to KCu₇S₄ was too large, the electrodes would mainly have exhibited the C properties, and the pseudocapacitance properties of the KCu₇S₄ may not be displayed. So the appropriate ratio of the C to KCu₇S₄ can help to improve the capacitance of the C/KCu₇S₄ hybrid ECs. All the results

show that the C/KCu₇S₄ hybrid ECs (1:10) exhibits the preferable electrochemical performance. The galvanostatic charging–discharging tests were obtained in a stable potential window of 0–0.8 V at a fixed current of 5 mA, and the results are presented in Fig. 4b. It shows good linear voltage–time profiles with small IR drops, and all of the charging curves are nearly symmetrical with their corresponding discharge counterparts, which indicate good capacitive behavior of the C/KCu₇S₄ hybrid structure. The areal capacitances of C/KCu₇S₄ hybrid ECs (1:5, 1:8, 1:10 and 1:15) also were achieved at various current, which are shown in Fig. 4c. The areal capacitance of C/KCu₇S₄ hybrid ECs (1:10) was as high as 469 mF cm⁻² (~ 300 F g⁻¹) at a current of 2 mA, which was higher than those for the C/KCu₇S₄ hybrid ECs 379 mF cm⁻² (1:5, ~ 243 F g⁻¹), 415 mF cm⁻² (1:8, ~ 266 F g⁻¹) and 431 mF cm⁻² (1:15, ~ 276 F g⁻¹), respectively. Remarkably, this value is also higher the values reported for other compositions, such as HZM electrodes (about 138.7 mF cm⁻² at 1 mA cm⁻²) [11], TiN@MnO₂ coaxial arrays (about 41 mF cm⁻² at 0.12 mA cm⁻²) [13], WO₃–_x@Au@MnO₂ nanowires (about 105 mF cm⁻² at 0.06 mA cm⁻²) [12], SnO₂@MnO₂ nanowires (about 64 mF cm⁻² at 0.08 mA cm⁻²) [14], hydrogenated TiO₂@MnO₂ nanowires (about 70 mF cm⁻² at 2 mA cm⁻²) [15], and PEDOT@MnO₂ nanoparticles (about 62 mF cm⁻² at 5 mA cm⁻²) [16], and even comparable to graphene sheets/Mn₃O₄ composites (about 242 mF cm⁻² at 1 mA cm⁻²) [17]. Specific energy and specific power are the two key factors for evaluating the power applications of electrochemical supercapacitors. A good electrochemical supercapacitor is expected to provide high energy density or high specific capacitance at high charging–discharging rates. Energy density (E) and Power density (P) can be calculated as $E = C_s V^2 / 2U$ (1) $P = E/t$ (2) where V is the cell voltage, C_s is total capacitance of the device, U is the device volume, and t is the discharge time [11]. The Ragone Plots clearly demonstrate the high power performance of the C/KCu₇S₄ hybrid ECs in Fig. 4d. The highest energy density of 8.14 mWh cm⁻³ and the maximum power density of 664.4 mW cm⁻³ were achieved.

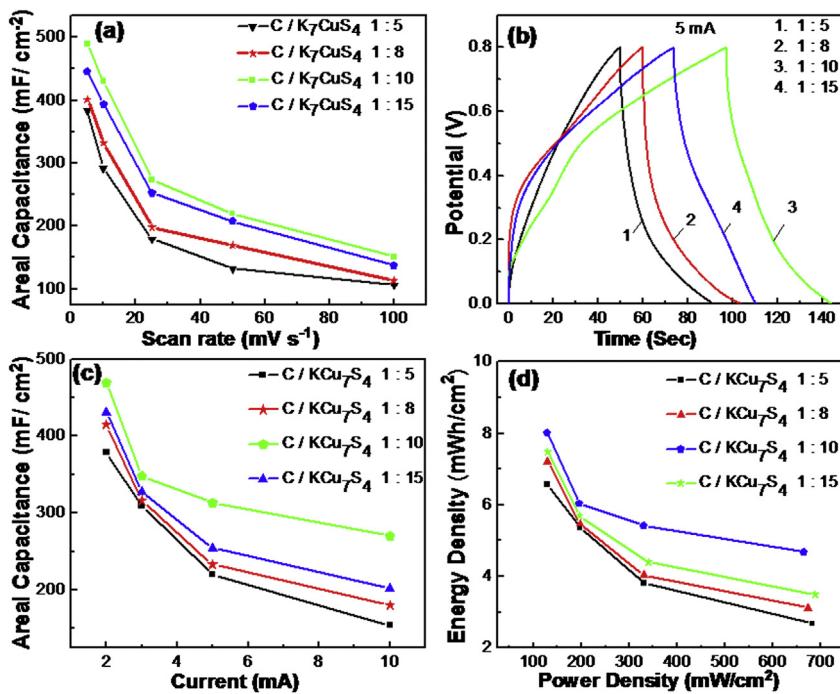


Fig. 4. (a) The areal capacitance of the different weight ratio of C/KCu₇S₄ hybrid ECs at different scan rates. (b) Galvanostatic charging–discharging curves for C/KCu₇S₄ hybrid ECs at a fixed current of 5 mA with the different weight ratio of C/KCu₇S₄ hybrid ECs. (c) The areal capacitance of the different weight ratio of C/KCu₇S₄ hybrid ECs at different charging–discharging of current (d) Ragone plot for C/KCu₇S₄ hybrid ECs.

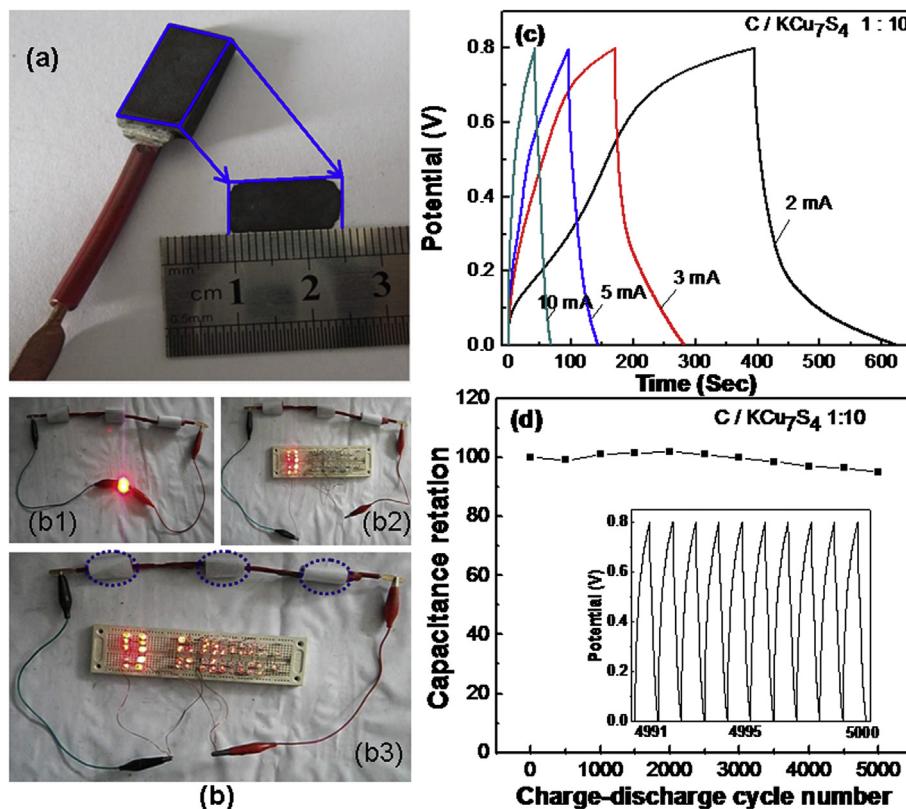


Fig. 5. Optical photographs of the C/KCu₇S₄ solid-state supercapacitor device. (a) Photograph of the capacitance region. The square indicates the capacitance region. (b) Photograph of the light-emitting-diodes (LEDs) driven by a device composed of three supercapacitors connected in series. (c) Galvanostatic charging–discharging curves for the C/KCu₇S₄ hybrid ECs at different current. (d) Cycling stability of C/KCu₇S₄ hybrid ECs (1:10) over 5000 cycles at a fixed current of 10 mA. The inset shows the galvanostatic charge/discharge curve for the device. (2 mA IR = 0.033 V, 3 mA IR = 0.045 V, 5 mA IR = 0.062 V, 10 mA IR = 0.071 V).

Furthermore, we had connected three supercapacitor units (1:10) in series to light a light-emitting diode (LED) well for about 5.5 min, 10 light-emitting diodes (LEDs) for 4 min, and 50 light-emitting diodes for 2.5 min after charging at 20 mA for 1 min (Fig. 5b) (The more details see the supporting information in Fig. S2). Fig. 5a indicates the capacitance region, every device has the same area of about 1.28 cm². Fig. 5c shows the galvanostatic charging–discharging curves for the C/KCu₇S₄ hybrid ECs at different current. The symmetrical triangles of the charge–discharge plots with small IR drops indicate an ideal electrochemical behavior of the C/KCu₇S₄ hybrid electrode. These results reveal the potential application of the C/KCu₇S₄ hybrid nanostructure supercapacitor device in energy storage. The long-term cycling stability of the C/KCu₇S₄ hybrid ECs was examined by a cyclic charge–discharge process at a fixed current of 10 mA in Fig. 5d. The specific capacitance of the C/KCu₇S₄ hybrid ECs (1:10) kept almost constant with slight fluctuations over 5000, which reveals the C/KCu₇S₄ hybrid ECs has a good long-term cyclic performance.

4. Conclusions

In summary, the KCu₇S₄ nanowires are a novel superionic conductive material, and it exhibits an extremely high ionic conductivity. In addition, the C/KCu₇S₄ hybrid ECs shows outstanding electrochemical performances with the largest specific capacitance of 469 mF cm⁻² (300 F g⁻¹) at the current of 2 mA, the highest energy density of 8.14 mWh cm⁻³ and the maximum power density of 664.4 mW cm⁻³. It retains 95% of its initial capacitance after 5000 times. Furthermore, they also can be used to fabricate a

simple solid-state capacitive device, and three hybrid ECs units in series to light a light-emitting diode (LED) for 5.5 min, 10 light-emitting diodes (LEDs) for 4 min, and 50 light-emitting diodes for 2.5 min. All these evidences indicate that the C/KCu₇S₄ hybrid nanostructure is very promising for the next generation high performance electrochemical supercapacitors.

Acknowledgments

This work has been funded by the National Natural Science Foundation of China (11204388), the Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP) (20120191120039, 20110191110034), the Fundamental Research Funds for the Central Universities (No. CDJRC10300001, No. CDJZR11300004, No. CDJZR12225501, No. CQDXWL-2013-012) and the large-scale equipment sharing fund of Chongqing University.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.138>.

References

- [1] G.P. Wang, L. Zhang, J.J. Zhang, Chem. Soc. Rev. 41 (2012) 797–828.
- [2] S. Hull, Rep. Progr. Phys. 67 (2004) 1233–1314.
- [3] D.T. Schoen, C. Xie, Y. Cui, J. Am. Chem. Soc. 129 (2007) 4116–4117.
- [4] R. Waser, M. Aono, Nat. Mater. 6 (2007) 833–840.
- [5] L. He, R. Mackay, S.J. Hwu, Y.K. Kuo, M.J. Skove, Y. Yokota, T. Ohtani, Chem. Mater. 10 (1998) 3172–3183.
- [6] S.J. Hwu, L. He, R. Mackay, Y.K. Kuo, M.J. Skove, M. Mahapatro, C.K. Bucher, J.P. Halladay, M.W. Hayes, Chem. Mater. 10 (1998) 6–9.

- [7] N.K. Kamaya, K.J. Homma, Y.C. Yamakawa, M.K. Hirayama, R.J. Kanno, M.S. Yonemura, T.K. Kamiyama, Y.K. Kato, S. Hama, K.J. Kawamoto, A. Mitsui, *Nat. Mater.* 10 (2011) 682–686.
- [8] S.G. Dai, Y. Xi, C.G. Hu, J.L. Liu, K.Y. Zhang, X.L. Yue, L. Chen, *J. Mater. Chem. A* 1 (2013) 15530–15534.
- [9] G.H. Yu, L.B. Hu, Michael Vosgueritchian, H.L. Wang, X. Xie, J.R. McDonough, X. Cui, Y. Cui, Z.N. Bao, *Nano Lett.* 11 (2011) 2905–2911.
- [10] H.L. Wang, Z.W. Xu, A. Kohandehghan, Z. Li, K. Cui, X.H. Tan, T.J. Stephenson, D. Mitlin, *ACS Nano* 7 (2013) 5131–5141.
- [11] P.H. Yang, X. Xiao, Y.Z. Li, Y. Dong, P.F. Qiang, X.H. Tan, W.J. Mai, Z.Y. Lin, W.Z. Wu, T.Q. Li, H.Y. Jin, P.Y. Liu, J. Zhou, C.P. Wong, Z.L. Wang, *ACS Nano* 7 (2013) 2617–2626.
- [12] X.H. Lu, T. Zhai, X.H. Zhang, Y.Q. Shen, L.Y. Yuan, B. Hu, L. Gong, J. Chen, Y.X. Gao, J. Zhou, Y.X. Tong, Z.L. Wang, *Adv. Mater.* 24 (2012) 938–944.
- [13] S. Dong, X. Chen, L. Gu, X. Zhou, L. Li, Z. Liu, P. Han, H. Xu, J. Yao, H. Wang, *Energy Environ. Sci.* 4 (2011) 3502–3508.
- [14] J. Yan, E. Khoo, A. Sumboja, P.S. Lee, *ACS Nano* 4 (2010) 4247–4255.
- [15] X. Lu, M. Yu, G. Wang, T. Zhai, S.Y. Tong, Y. Ling, Y. Li, *Adv. Mater.* 25 (2013) 267–272.
- [16] R. Liu, J. Duay, S.B. Lee, *ACS Nano* 4 (2010) 4299–4307.
- [17] J.W. Lee, A.S. Hall, J.D. Kim, T.E. Mallouk, *Chem. Mater.* 24 (2012) 1158–1164.